

Applicants : Chyi-Shan Wang, Max Alexander, Jr.
Serial No. : 10/698,218
Filed : October 31, 2003
Title : CONDUCTIVE POLYMERIC NANOCOMPOSITE MATERIALS
Docket No. : UVD 0307 VA
Examiner : M. Kopec
Art Unit : 1751

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

DECLARATION OF CHYI-SHAN WANG AND MAX ALEXANDER, JR.
UNDER 37 CFR §1.131

We, Chyi-Shan Wang and Max Alexander, Jr., declare and state as follows:

We are co-inventors of the above-identified patent application which is assigned to the University of Dayton. We are familiar with the Office Action mailed July 15, 2004, including the rejections made by the Examiner therein. We are also familiar with the references cited by the Examiner in that Office Action, including U.S. Publication No. 2003/0089890 to Niu et al.

On a date prior to July 11, 2001, the filing date of the Niu et al. publication, we had jointly conceived of the subject matter of claims 1-6 of this patent application and had jointly reduced such subject matter to practice. All of the acts reported below were carried out in the United States. As evidence of the conception and reduction to practice of the invention, we submit the following exhibit. As permitted by present practice, dates contained in the exhibit have been obscured.

Exhibit A is an invention disclosure submitted to the University of Dayton by us on a date prior to July 11, 2001. The disclosure describes a method for uniformly dispersing vapor-grown carbon nanofibers into polymer matrices to form a nanocomposite material having enhanced mechanical strength, dimensional stability, and electrical and thermal conductivity. The disclosure further describes mixing carbon nanofibers with a polymer and various solvents to achieve a solution mixture followed by evaporating the solvent. Table 2 illustrates the electrical conductivity of various nanocomposite films produced using the method.

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful and false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application and any patent issued thereon.



Chyi-Shan Wang

Max Alexander, Jr.

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful and false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application and any patent issued thereon.

Chyi-Shan Wang

Max D. Alexander Jr.

Max Alexander, Jr.

Disclosure No. 320

Log-In-Date _____

OFFICE USE ONLY

UNIVERSITY OF DAYTON TECHNOLOGY DISCLOSURE FORM - INVENTIONS

1. Descriptive title of invention Method for Forming Conductive Polymer-based Nanocomposite Materials Using Carbon Nanofibers

2. Inventor(s)

Name (typed) Chyi-Shan Wang
Signature *Chyi-Shan Wang*
Date _____
Employer University of Dayton

Business Phone No. (937)255-9161
Home Address 1961 N Springcrest Court
Beavercreek, OH 45432

Name (typed) Max Alexander
Signature *Max D. Alexander*
Date _____
Employer Department of Defense -Air Force

Business Phone No. (937)255-9135
Home Address 1069 Cambridge-Station Rd
Centerville, OH 45458

Name (typed) _____
Signature _____
Date _____
Employer _____
Business Phone No. _____
Home Address _____

Name (typed) _____
Signature _____
Date _____
Employer _____
Business Phone No. _____
Home Address _____

3. Witness: This disclosure shall be signed by two witnesses who are not inventors of any part of this invention.

Name (Typed) William E. Click
Signature *William E. Click*
Date _____

Name (Typed) Barney Taylor
Signature *Barney E Taylor*
Date _____



4. Approval: The disclosure shall be signed by the Research Institute Division Head and/or the Academic Department Chair as applicable.

Name (typed) Allan Crasto

Name (typed) _____

Title Division Head

Title _____

Signature 

Signature _____

Date _____

Date _____

5. Was the work leading to the invention performed (in whole or in part) on an externally sponsored program? YES X NO _____

Sponsoring Agency/Firm Air Force Research Laboratory

Account Number 1207030312 Contract Number F33615-95-D-5044

6. Date and circumstances of first verifiable record of the invention:

On _____, a film containing 16.7 wt% of an AG (as-grown) grade carbon nanofiber in thermoplastic polyurethane was cast from a 10 wt% DMSO solution mixture. This film exhibited an electrical conductivity of 0.25 S/cm (UDRI notebook #711 page 60-61).

7. Date and description of other written records of the invention predating this disclosure:

More test results, including electrical conductivity, of various nanocomposite samples were recorded by Max Alexander in UDRI notebook #742 page 41-47 on _____

8. Is there a laboratory notebook record of this invention? YES X NO _____

Notebook number and other identification: UDRI Notebook #711 page 60-61 (issued to Chyi-

Page numbers: Shan Wang) and UDRI Notebook #742, page 41-47 (issued to Max Alexander)

9. Has the invention been reduced to practice? YES X NO _____

Date _____ Where and How Wright-Patterson AFB

Sheets of the conductive polymer nanocomposite material have been cast from solution mixtures.

The sheets have been also cut into smaller pieces and fed through an extruder to form filaments,

which have been used to conduct current to light photodiodes. Subsequently, various solution

mixtures have been prepared for fabricating conductive polymer-based thin films by spin coating,

dip coating and coagulation methods.

10. First Public Disclosure

Identify the names, places, and dates associated with the first disclosure of pertinent details of the invention to anyone outside the University without the benefit of a formal confidentiality agreement. Public disclosure may be made in the following ways: (1) an oral presentation to a scientific meeting or an informal group; (2) circulation of an abstract of a talk; (3) publication of a journal article or news story; (4) delivery and distribution of a contract report, etc. Attach copies of any publications. If you are not sure whether public disclosure has been made, give the details of all external communication concerning the invention. If there has been no outside disclosure, so indicate.

N/A

11. Sale of Product. Has a purchase order been accepted for sale of the result of the invention in any form? YES _____ NO X

If YES, please provide pertinent details. _____

12. Samples. Have samples of the invention been given to anyone outside the University for evaluation (including any sponsors)? YES X NO _____

Please provide pertinent details. Samples have been provided to the Air Force Research Laboratory for conductivity measurement.

13. What do you see as the commercial value of the invention? What is the market and how large is it? The present invention provides a method for producing a variety of cost-effective, polymer-based conductive nanocomposite materials, including paints, coatings, caulk, sealant, adhesives, fibers, thin films, thick sheets, tubes, and large structural components. These materials have applications in space, aerospace, automotive, chemical and other industries for thermal management, electromagnetic interference shielding, electrostatic discharge and various electro- optical devices such as photovoltaic cells. Its market size is expected to be very large.
-
-
-

14. List the names of any firms that might be interested in licensing the invention.

Motorola, GE and Boeing.

15 Inventors' roles.

On _____ Max Alexander of the US Air Force invited Chyi-Shan Wang of the
University of Dayton Research Institute to collaborate on a project by infiltrating thermoplastic
polyurethane with conductive metals to fabricate conductive elastomers. Chyi-Shan Wang
conducted the research and conceived the idea of using carbon nanotubes and carbon nanofibers,
instead of metals, as the conducting phase in the elastomer. Through further discussion and
experiment, the collaboration led to the current invention.

METHOD FOR FORMING CONDUCTIVE POLYMER-BASED NANOCOMPOSITE MATERIALS USING CARBON NANOFIBERS

Nonconfidential Abstract

A method is provided for forming a conductive, polymer-based nanocomposite material, in which a continuous network of vapor-grown carbon nanofibers is inserted via a solution state of the polymer to impart significant electrical conductivity. It has been shown that such a polymer nanocomposite material based on thermoplastic polyurethane is conductive at less than 1% by volume of the carbon nanofibers, and the conductivity drastically increases to great than 20 S/cm at 15.4% by volume of the nanophase inclusion. This polymer nanocomposite material is two to three orders of magnitude more conductive than that prepared by the conventional polymer melt blending method at the same carbon nanofiber concentration and can be further processed into various shapes and sizes using conventional extrusion and molding techniques without losing conductivity. The present invention can be used not only to confer electrical conductivity to a variety of polymeric materials, such as paints, coatings, caulks, sealant, adhesives, fibers, thin films, thick sheets, tubes, and large structural components, but also to enhance their heat transfer and mechanical performance. The conductive polymer-based nanocomposite material will have applications in space, aerospace, electronic, automotive and chemical industries for thermal management, electromagnetic interference shielding, electrical signal transfer, electrostatic painting of panels, electrostatic discharge and opto-electronic devices such as photovoltaic cells.

BACKGROUND OF THE INVENTION

The present invention relates to a method for fabricating a polymer-based nanocomposite material in which a conductive network of vapor-grown carbon nanofibers is inserted to impart significant mechanical strength, dimensional stability, and electrical as well as thermal conductivity. The conductive nanocomposite material is achieved by dispersing the carbon nanofibers via a solution state of the polymer, followed by removing the solvent through evaporation or coagulation.

Vapor-grown carbon nanofibers are a unique form of carbon produced by a variation of the vapor-phase catalytic method, in which a carbon-containing feedstock is pyrolyzed in the presence of small metal catalyst particles. Figure 1 shows the scanning electron microscope (SEM) image of an as-grown (AG grade) carbon nanofibers. The nanofibers typically have an outer diameter of 60 - 200 nm, a hollow core of 30 - 90 nm, and a length on the order of 50 -100 microns. Figure 2 shows the transmission electron microscope (TEM) image of such a carbon nanofiber. The light phase on the right of the image is the hollow core. In the middle of the image is the edge view of the highly ordered graphitic planes. This structure resembles that observed from multi-walled carbon nanotubes. The gray region to the left of the image is the less ordered chemical-vapor-deposited (CVD) carbon. However, a heat treatment to 3000 °C can greatly increase the order of the CVD carbon, giving rise to substantially improved mechanical,

electronic and thermal transport properties. Table 1 compares the properties of the as-grown carbon nanofibers with those of heat-treated (HT grade) species.

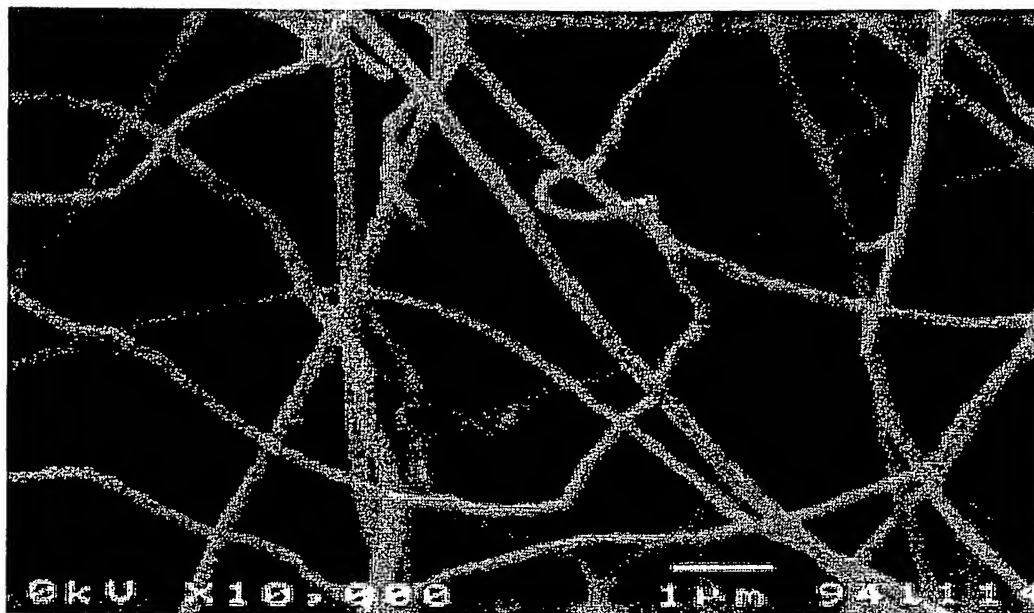


Figure 1. SEM image of as-grown carbon nanofibers.

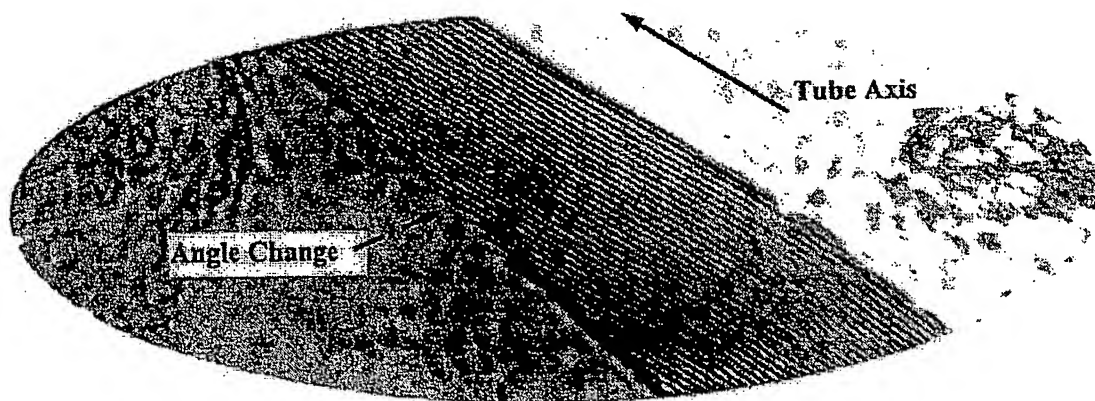


Figure 2 TEM image of the wall of an as-grown carbon nanofiber: the light phase to the right is the hollow core, the parallel lines at center are the graphitic planes, and at left is less ordered CVD carbon.

Table 1. Properties of vapor-grown carbon nanofibers.

Property	As Grown	Heat Treated	Units
Tensile Strength	2.7	7.0	GPa
Tensile Modulus	400	600	GPa
Ultimate Strain	1.5	0.5	%
Density	1.8	2.1	g/cm^3
Electrical Resistivity	1000	55	$\mu\Omega\text{-cm}$
Thermal Conductivity	20	1950	W/m-K

Figure 3 compares the electronic and thermal transport properties of carbon nanofibers to those of other commercially available carbon fibers and various metals. It shows that heat-treated carbon nanofibers have an electrical conductivity approaching that of highly ordered pyrolytic graphite and a thermal conductivity that is five times as high as that of copper. Therefore, vapor-grown carbon nanofibers can be an excellent candidate for conferring desired properties such as mechanical strength, stiffness, electrical and thermal conductivity, and dimensional stability (e.g., reduced coefficient of thermal expansion) to polymers.

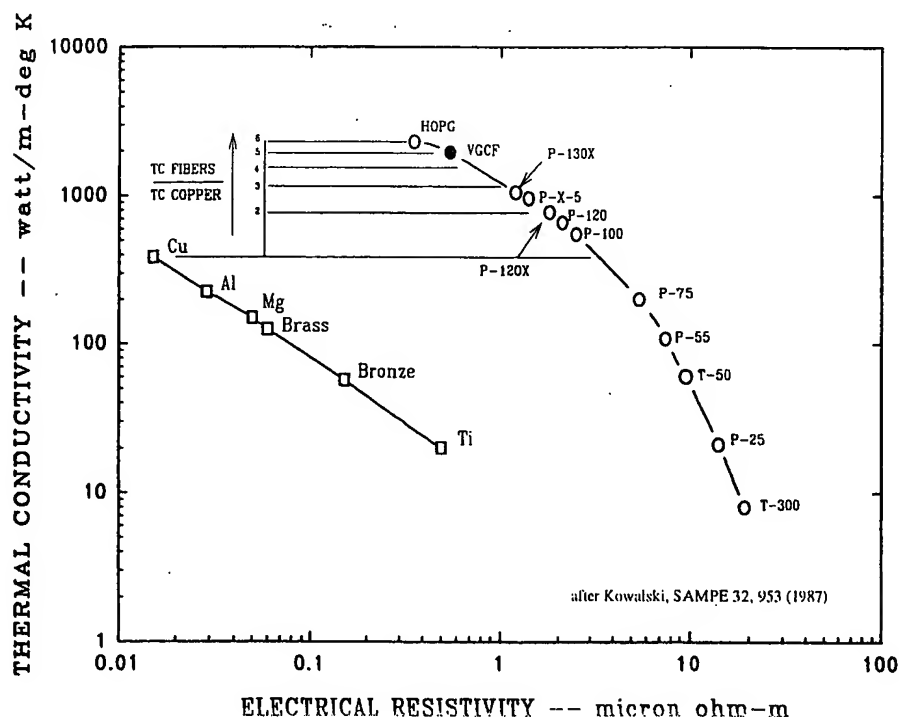


Figure 3. Comparison of transport properties of vapor-grown carbon nanofibers (VGCF) to those of commercial carbon fibers, metals, and highly ordered pyrolytic graphite (HOPG).

Previously, the dispersion of vapor-grown carbon nanofibers in polymer matrices has been accomplished by polymer melt blending method. This processing method relies on the ability to mechanically shear apart the dispersants in the polymer matrix of interest. Since most polymers are incompatible with the carbon nanofibers, it is difficult to achieve nanoscale dispersion of the carbon nanofibers in the polymer matrix. Furthermore, the high shear mechanical blending can result in the breakage of the carbon nanofibers. Therefore, the composite material prepared by the melt blending method does not afford the maximum reinforcement efficiency of the carbon nanofibers.

SUMMARY OF THE INVENTION

The present invention provides a method for uniformly dispersing vapor-grown carbon nanofibers into polymer matrices to enhance their performance in mechanical strength, dimensional stability, and electrical and thermal conductivity. In this method, the uniform dispersion of the carbon nanofibers in a specific polymer matrix is achieved via a solution state of the polymer, followed by evaporation or coagulation of the solvent to reduce the nanocomposite material.

It is shown that the polymer nanocomposite material produced by the present method is normally two to three orders of magnitude more conductive than that produced by the polymer melt blending method, when the same amount of the carbon nanofibers is used. It is also found that the current polymer nanocomposite material has a very low electronic conducting percolation threshold, less than 1% by volume of the carbon nanofibers, indicative of an extremely large aspect ratio of the carbon nanofibers. These observations suggest that the present method is not only more effective in dispersing the carbon nanofibers in polymer matrices but also in preserving their large aspect ratio of length to diameter than the conventional polymer melt blending method.

To maintain the large aspect ratio of the carbon nanofibers during processing is important to some applications, particularly for elastomeric polymers that are used to form gaskets or seal seams structures. Such materials depend on high resilience and deformability to perform their function. Metal particles have high intrinsic conductivity, but they require a very high loading to form a conductive network in these materials due to their small aspect ratio. The high loading of metal particles normally degrades the polymer's qualities, limiting their performance, reliability, and life span. Therefore, the low conducting percolation threshold afforded by the carbon nanofibers of large aspect ratios can ensure a better overall product for shielding and charge dissipation applications.

The present invention is capable of producing an unusually uniform solution mixture of the vapor-grown carbon nanofibers and their polymer matrices. The solution mixture may be used for conductive paints, coatings, fibers, thin films, thick sheets, tubes, seals, or large structural components using processing techniques such as casting, spraying and extrusion. Once the solvent is removed, the polymer nanocomposite material can be further processed into various shapes by conventional extrusion and molding techniques without losing its conductivity.

Furthermore, the thermal, mechanical and electrical properties of the nanocomposite material can be tailored by using different types and quantities of the carbon nanofibers for thermal management, EMI shielding, electrical signal and power transfer, electrostatic painting of panels, electrostatic discharge, conformal conductive coatings and opto-electronic device applications.

According to one aspect of the present invention, a method for forming a conductive polymer nanocomposite material is provided comprising the steps of providing a polymer, mixing vapor-grown carbon nanofibers with the polymer in a solvent of the polymer to form a uniform solution mixture, and removing the solvent from the solution mixture such that the polymer nanocomposite material is produced. Depending on specific polymer and solvent systems, the solvent removal may be accomplished by evaporation or coagulation in a nonsolvent. The carbon nanofibers are preferentially selected from the group of large aspect ratios of length to diameter. In a preferred embodiment for high conductivity and low carbon nanofiber loading, the carbon nanofibers are fully graphitized by heat treatment to 3000°C.

DETAILED DESCRIPTION

The method of the present invention provides a process that allows vapor-grown carbon nanofibers to be uniformly dispersed in a polymer matrix to confer significant mechanical, thermal and electronic transport properties. While carbon nanofibers themselves alone do not disperse well in organic solvents, it is found that they disperse very well with the presence of a polymer. Therefore, the concept of dispersing carbon nanofibers via a solution state of the polymer is conceived to impart mechanical and transport properties to polymers. The mechanical and transport properties of the resulting polymer nanocomposite material can be tailored by using different types and amounts of the carbon nanofibers. The present method uses a low-temperature solution-processing scheme to uniformly disperse the carbon nanofibers. It does not require the high shear mixing of the polymer melt at elevated temperatures, which usually degrades the aspect ratio of the carbon nanofibers leading to inferior reinforcement in mechanical and transport properties.

Different types and amounts of the carbon nanofibers may be utilized to tailor the mechanical and transport properties of the nanocomposite material for a wide range of applications. These include EMI shielding (greater than 1 S/cm), electrostatic painting of panels (10^{-4} to 10^{-6} S/cm), and electrostatic discharge (10^{-8} to 10^{-10} S/cm). Depending on specific polymer and solvent systems as well as desired application techniques, the solvent may be removed by evaporation or coagulation method.

In order for the invention to be more readily understood, reference is made to the following examples, which are intended to be illustrative of the invention, but are not intended to be limiting in scope.

Example 1 - Nanocomposite material of thermoplastic polyurethane and as-grown (AG) carbon nanofibers prepared from a solution mixture in dimethyl sulfoxide (DMSO)

A solution mixture is prepared by mixing 0.2 grams of an AG carbon nanofiber and 1.00 gram of a thermoplastic polyurethane in 10.00 grams of DMSO in a closed glass container. The mixture is then agitated with a magnetic stir bar. A thin film is cast from the solution mixture by evaporating the solvent at a moderately high temperature on a hot plate. The polymer nanocomposite film is further dried in a vacuum oven at 80°C under reduced pressure. This film has a concentration of 16.7% by weight and 11.7% by volume of the carbon nanofibers and exhibits an electrical conductivity of 0.25 S/cm.

Example 2 - Nanocomposite material of thermoplastic polyurethane and heat-treated (HT) carbon nanofibers prepared from a solution mixture in DMSO

A solution mixture is prepared by mixing 0.2 grams of a heat-treated (HT) carbon nanofiber and 1.00 gram of a thermoplastic polyurethane in 10.00 grams of DMSO in a closed glass container. The mixture is then agitated with a magnetic stir bar. A thin film is cast from the solution mixture by evaporating the solvent at a moderately high temperature on a hot plate. The polymer nanocomposite film is further dried in a vacuum oven at 80°C under reduced pressure. This film has a concentration of 16.7% by weight and 10.2% by volume of the carbon nanofibers and exhibits an electrical conductivity of 5.5 S/cm. This film retains a conductivity of 1.3 S/cm at 100% elongation (stretched to twice its original length).

Example 3 - Nanocomposite material of thermoplastic polyurethane and heat-treated (HT) carbon nanofibers prepared from a solution mixture in tetrahydrofuran (THF)

As shown in Table 2, a series of solution mixtures of a thermoplastic polyurethane and a heat-treated carbon nanofiber are prepared in THF using the method described in examples 1 and 2. Thin films are cast from these solution mixtures by evaporating the solvent at room temperature. Also included in Table 2 are the conductivity values of these films in relation to their concentration of the carbon nanofibers, where the volume percentage is calculated based on the density (obtained from the manufacturers) of 1.19 g/cm³ for the polyurethane and 2.1 g/cm³ for the heat-treated carbon nanofiber. Figure 5 shows that the polymer nanocomposite material has a conducting percolation threshold less than 1.0% by volume concentration of the carbon nanofiber.

Figure 6 shows the tensile mechanical properties of the nanocomposite films of different concentrations of the carbon nanofibers. It clearly demonstrates that both tensile strength and stiffness of the films are substantially improved with increasing the carbon nanofiber content. Therefore, the nanocomposite material affords superior mechanical durability and dimensional stability to the pristine polyurethane. The ultimate elongation of these nanocomposite films ranges from 600% to 1000%, comparable to that of the pristine polyurethane. This indicates an extremely uniform dispersion of the carbon nanofiber in the polymer matrix. Except for the most dilute films, most films remain conductive even after fracture.

Table 2. Conductivity of polyurethane nanocomposite films in relation to the concentration of heat-treated (HT) carbon nanofibers.

Nanofiber (g)	Polyurethane (g)	THF (g)	wt%	vol%	Conductivity (S/cm)
0.020	1.00	10.0	1.96%	1.12%	0.0038
0.040	1.00	10.0	3.85%	2.22%	0.10
0.080	1.00	10.0	7.41%	4.34%	0.54
0.120	1.00	10.0	10.7%	6.37%	1.14
0.160	1.00	10.0	13.8%	8.31%	3.93
0.200	1.00	10.0	16.7%	10.2%	4.69
0.240	1.00	10.0	19.4%	12.0%	8.70
0.280	1.00	10.0	21.9%	13.7%	16.6
0.320	1.00	10.0	24.2%	15.4%	20.8

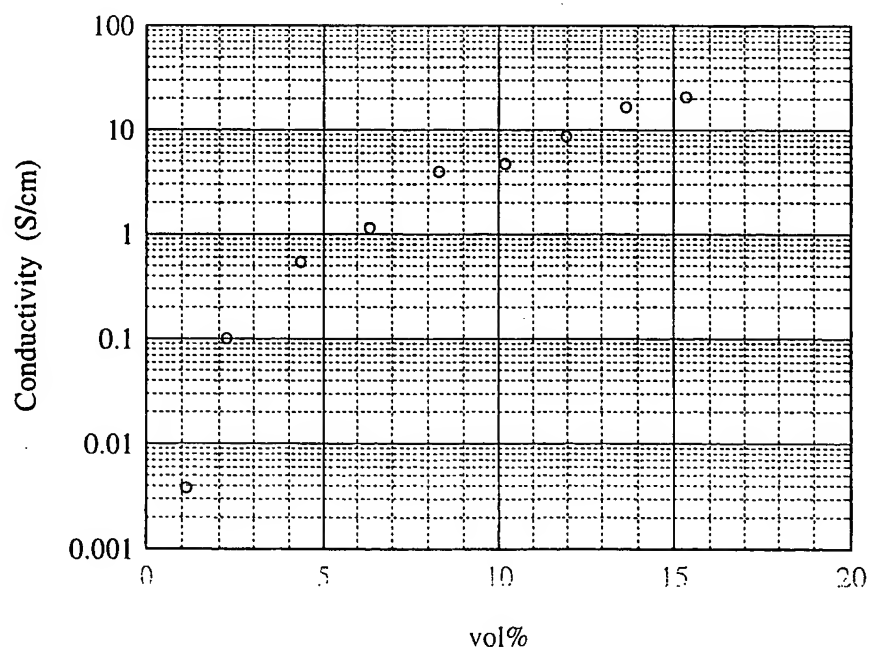


Figure 5. Conductivity of the nanocomposite material in relation to their carbon nanofiber concentration.

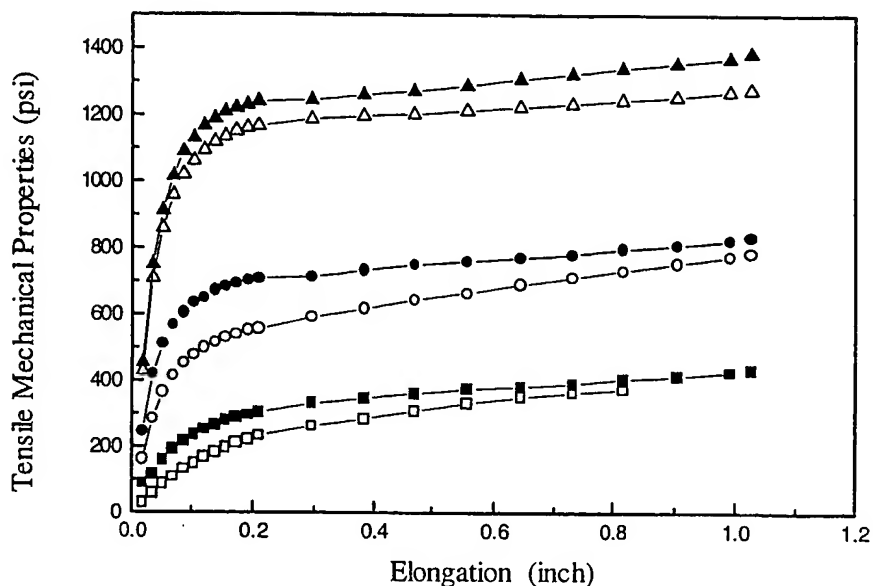


Figure 6. Tensile mechanical properties of the nanocomposite material of carbon nanofibers and polyurethane; the curves from bottom up have a concentration of 0, 2.22, 4.34, 6.37, 10.2, and 12.0% by volume of the carbon nanofiber, respectively.

Example 4 - Nanocomposite material of thermoplastic polyurethane and heat-treated (HT) carbon nanofibers prepared by melt blending method.

20 grams of the HT carbon nanofiber and 100 grams of the thermoplastic polyurethane are mixed in a Haake Rheomixer at 150°C for 2 hours. The resulting composite material is pressed into a thin film with heat. This film has a concentration of 16.7% by weight and 10.2% by volume of the carbon nanofibers and exhibits an electrical conductivity from 0.0052 to 0.0098 S/cm. These conductivity values are two to three orders of magnitude lower than that of the nanocomposite film that contains the same concentration of the carbon nanofiber but is prepared by the current solution dispersion method.

Example 5 - Nanocomposite material of polyimide/amic acid and heat-treated carbon nanofibers prepared from a solution mixture in N,N-dimethyl acetamide (DMAc).

A solution mixture is prepared by mixing 0.202 grams of heat-treated carbon nanofibers and 1 gram of polyimide/amic acid in 10.0 grams of DMAc in a closed glass container. The mixture is then agitated with a magnetic stir bar. A thin film is prepared from the solution mixture by evaporating the solvent at 60°C. The film is further dried in a vacuum oven at 200°C

for 2 hours. This film has a concentration of 16.8% by weight of the carbon nanofibers and exhibits an electrical conductivity from 1.7 to 2.8 S/cm.

Another solution mixture of 0.302 gram of heat-treated carbon nanofibers and 1.0 gram of polyimide/amic acid is prepared in 10.0 grams of DMAc using the same method. The solution mixture is then cast into a film by evaporating the solvent at 60°C. The film is further dried in a vacuum oven at 200°C for 2 hours. This film has a concentration of 23.2% by weight of the carbon nanofibers and exhibits an electrical conductivity from 5.1 to 7.7 S/cm.

Example 6 - Nanocomposite material of ladder polymer poly(benzimidazobenzophenanthroline) (BBL) and heat-treated carbon nanofibers prepared from a solution mixture in methanesulfonic acid (MSA).

A solution mixture is prepared by mixing 0.02 grams of HT carbon nanofiber and 0.1 grams of BBL in 20 grams of MSA in a closed glass container. The solution mixture is then agitated with a magnetic stir bar. The solution mixture is doctor-bladed into a film on a glass slide and subsequently immersed in water to coagulate the nanocomposite film. The nanocomposite film is then air-dried at room temperature. This film has a concentration of 16.7% by weight and an electrical conductivity of 1.0 S/cm.

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the methods and apparatus disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

CLAIMS

What is claimed is:

1. A method for forming a conductive polymer nanocomposite material using carbon nanofibers comprising the steps of:
providing a polymer;
mixing the carbon nanofibers with the polymer in a solvent of the polymer;
removing said solvent such that the nanocomposite material is reduced.
2. The method of claim 1 in which said polymer is a thermoplastic.
3. The method of claim 1 in which said polymer is a thermoset.
4. The method of claim 1 in which said polymer is a high temperature polymer that is not feasible for melt processing, such as polyimides and aromatic-heterocyclic rigid-rod and ladder polymers.
5. The method of claim 1 in which said carbon nanofibers are vapor-grown carbon nanofibers.

6. The method of claim 4 in which said carbon nanofibers are as-grown vapor-grown carbon nanofibers.
7. The method of claim 4 in which said carbon nanofibers are pyrolytically stripped vapor-grown carbon nanofibers.
8. The method of claim 4 in which said carbon nanofibers are heat-treated vapor-grown carbon nanofibers.
9. The method of claim 1 in which said solvent is a solvent of said polymer.
10. The method of claim 4 in which said solvent is preferably to be polar solvents.
11. The method of claim 1 in which said solvent is removed by evaporation.
12. The method of claim 11 in which said solvent is evaporated upon painting.
13. The method of claim 11 in which said solvent is evaporated upon spraying.
14. The method of claim 11 in which said solvent is evaporated upon spin coating.
15. The method of claim 11 in which said solvent is evaporated upon casting.
16. The method of claim 1 in which said solvent is removed by coagulation.
17. The method of claim 1 in which said composite materials is in the form of a fiber.
18. The method of claim 1 in which said composite materials is in the form of a thin film.
19. The method of claim 1 in which said composite materials is in the form of a thick sheet.
20. The method of claim 1 in which said composite materials is in the form of a tube.
21. The method of claim 1 in which said composite materials is in the form of a large bulk structure.
22. The method of claim 1 in which said composite materials is in the form of a coating.
23. The method of claim 1 in which said composite materials is in the form of a caulking material.
24. The method of claim 1 in which said nanocomposite materials can be further processed into various forms by extrusion and molding techniques.
25. The method of claim 19 in which said composite materials can be reprocessed into fibers.
26. The method of claim 19 in which said composite materials can be further into thin films.
27. The method of claim 19 in which said composite materials can be further processed into thick sheets.
28. The method of claim 16 in which said composite materials can be further processed into tubes.
29. The method of claim 16 in which said composite materials can be further processed into large bulk structures.